

WE CLAIM:

1. A process for patterning a substrate, comprising:
 - (a) coating the substrate with a film of a photoresist composition comprised of (i) a polymer that is rendered soluble in aqueous base at a temperature of less than about 100°C by acid-catalyzed deprotection of pendent acetal- or ketal-protected carboxylic acid groups, and (ii) a photoacid generator;
 - (b) patternwise exposing the film to an imaging radiation source so as to form a latent, patterned image in the film;
 - (c) baking the exposed film at a post-exposure bake temperature below about 100°C; and
 - (d) developing the latent image with a developer to form a patterned substrate.
2. The process of claim 1, wherein the radiation is electron-beam, x-ray, ultraviolet, or extreme ultraviolet radiation.
3. The process of claim 2, wherein the radiation is ultraviolet radiation.
4. The process of claim 3, wherein the ultraviolet radiation has a wavelength of 193 nm, 157 nm, or 13.4 nm.
5. The process of claim 4, wherein the ultraviolet radiation has a wavelength of 193 nm.
6. The process of claim 4, wherein the ultraviolet radiation has a wavelength of 157 nm.

7. The process of claim 1, further comprising etching the patterned substrate.
8. The process of claim 7, wherein the etching comprises ion etching.
9. The process of claim 1, wherein the film is insoluble in aqueous base, and wherein the imaging radiation renders the film soluble in the aqueous base where exposed to the imaging radiation source.
10. The process of claim 9, further comprising removing the soluble portions of the film.
11. The process of claim 1, wherein the substrate is ceramic, metallic, semiconductive, or a combination thereof.
12. The process of claim 1, wherein the substrate comprises a silicon wafer, a photolithographic mask blank, or a printed circuit board.
13. The process of claim 1, wherein the substrate comprises silicon dioxide, silicon nitride, silicon oxynitride, or a combination thereof.
14. The process of claim 1, further comprising, before exposure of the film in (b), performing a prebake of the film at a temperature and for a time sufficient to remove residual solvent.

15. The process of claim 14, wherein the prebake temperature is below about 130°C.
16. The process of claim 1, wherein the post-exposure bake temperature is between about 25°C and about 100°C.
17. The process of claim 16, wherein the post-exposure bake temperature is between about 25°C and about 80°C.
18. The process of claim 17, wherein the post-exposure bake temperature is between about 25°C and about 50°C.
19. The patterned substrate prepared by the process of claim 1.
20. The process of claim 1, wherein the polymer is prepared by polymerization of a monomer mixture, the mixture comprising:
- (a) at least one first olefinic monomer containing an acetal or ketal linkage, the acid-catalyzed cleavage of which renders the polymer soluble in aqueous base; and
 - (b) at least one second olefinic monomer selected from (i) an olefinic monomer containing a pendant fluorinated hydroxyalkyl group R^H , (ii) an olefinic monomer containing a pendant fluorinated alkylsulfonamide group R^S , and (iii) combinations thereof.

21. The process of claim 20, wherein the acetal or ketal linkage is contained within an acid-cleavable group R^{CL} in the first olefinic monomer, the acid-cleavable group having the structure



in which:

m, n, and q are independently zero or 1;

L^1 is selected from C_1 - C_{12} alkylene, substituted C_1 - C_{12} alkylene, C_1 - C_{12} heteroalkylene, substituted C_1 - C_{12} heteroalkylene, and further wherein when L^1 is optionally substituted and/or heteroatom-containing C_1 - C_{12} alkylene, L^1 may be linear, branched, or cyclic;

X is selected from C_3 - C_{30} alicyclic and substituted C_3 - C_{30} alicyclic;

L^2 is selected from C_1 - C_{12} alkylene, substituted C_1 - C_{12} alkylene, C_1 - C_{12} heteroalkylene, substituted C_1 - C_{12} heteroalkylene, and further wherein when L^2 is optionally substituted and/or heteroatom-containing C_3 - C_{12} alkylene, L^2 may be linear, branched, or cyclic; and

R^1 is selected from acetal-containing and ketal-containing substituents.

22. The process of claim 20, wherein R^H has the structure $-L^3-CR^{11}R^{12}-OH$, in which:

L^3 is selected from C_1 - C_{12} alkylene, substituted C_1 - C_{12} alkylene, C_1 - C_{12} heteroalkylene, substituted C_1 - C_{12} heteroalkylene, C_3 - C_{15} alicyclic, C_3 - C_{15} fluoroalicyclic, and combinations thereof;

R^{11} is selected from hydrogen, C_1 - C_{24} alkyl, and substituted C_1 - C_{24} alkyl; and

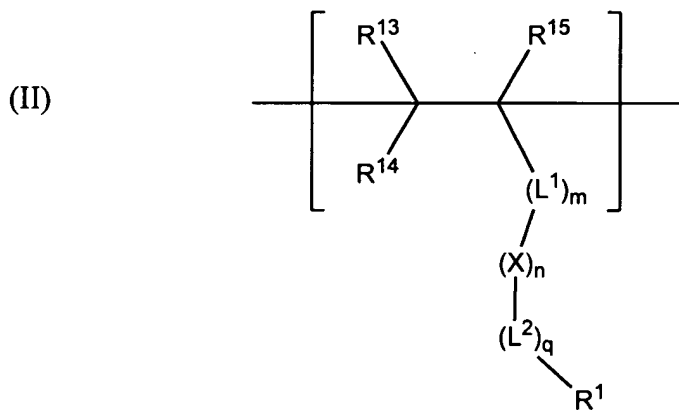
R^{12} is C_1 - C_{24} alkyl or fluorinated C_1 - C_{24} alkyl, with the proviso that at least one of R^{11} and R^{12} is fluorinated; and further wherein R^{11} and R^{12} can be taken together to form a ring.

23. The process of claim 20, wherein R^S has the structure $-L^3-SO_2-NHR^{16}$, in which:

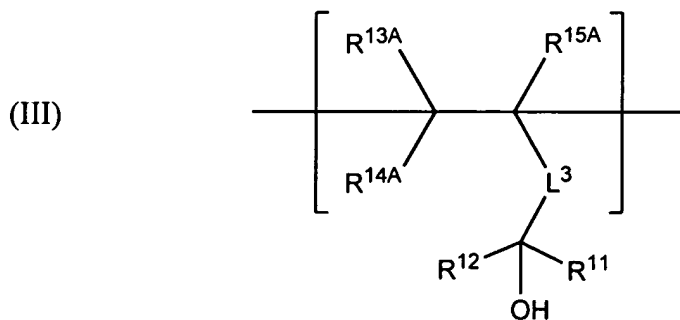
L^3 is selected from C_1 - C_{12} alkylene, substituted C_1 - C_{12} alkylene, C_1 - C_{12} heteroalkylene, substituted C_1 - C_{12} heteroalkylene, C_3 - C_{15} alicyclic, C_3 - C_{15} fluoroalicyclic, combinations thereof; and

R^{16} is selected from C_1 - C_{24} alkyl and substituted C_1 - C_{24} alkyl, C_1 - C_{24} fluoroalkyl and substituted C_1 - C_{24} fluoroalkyl.

24. The process of claim 20, wherein the polymer comprises a first olefinic monomer unit having the structure of formula (II)



and a second olefinic monomer unit having the structure of formula (III)



wherein:

m, n, and q are independently zero or 1;

L^1 is selected from C_1 - C_{12} alkylene, substituted C_1 - C_{12} alkylene, C_1 - C_{12} heteroalkylene, substituted C_1 - C_{12} heteroalkylene, and further wherein when L^1 is optionally substituted and/or heteroatom-containing C_1 - C_{12} alkylene, L^1 may be linear, branched, or cyclic;

X is selected from C_3 - C_{30} alicyclic and substituted C_3 - C_{30} alicyclic;

L^2 is selected from C_1 - C_{12} alkylene, substituted C_1 - C_{12} alkylene, C_1 - C_{12} heteroalkylene, substituted C_1 - C_{12} heteroalkylene, and further wherein when L^2 is optionally substituted and/or heteroatom-containing C_3 - C_{12} alkylene, L^2 may be linear, branched, or cyclic; and

R^1 is selected from acetal-containing and ketal-containing substituents;

L^3 is selected from C_1 - C_{12} alkylene, substituted C_1 - C_{12} alkylene, C_1 - C_{12} heteroalkylene, substituted C_1 - C_{12} heteroalkylene, C_3 - C_{15} alicyclic, C_3 - C_{15} fluoroalicyclic and combinations thereof;

R^{11} is selected from hydrogen, C_1 - C_{24} alkyl, and substituted C_1 - C_{24} alkyl;

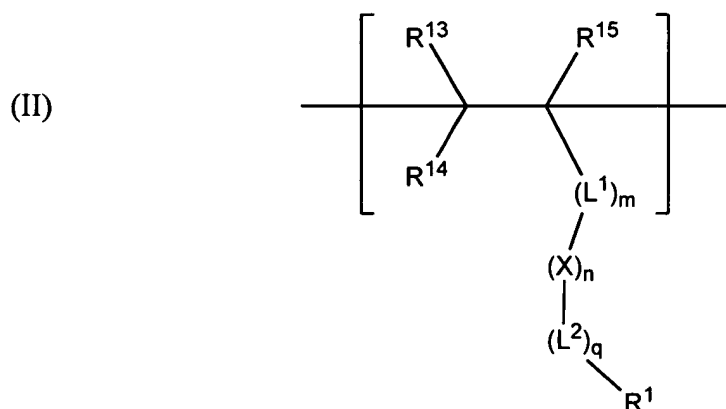
R^{12} is C_1 - C_{24} alkyl or fluorinated C_1 - C_{24} alkyl, with the proviso that at least one of R^{11} and R^{12} is fluorinated; and further wherein R^{11} and R^{12} can be taken together to form a ring;

R^{13} and R^{13A} are independently selected from hydrogen, fluorine, C_1 - C_{24} alkyl, substituted C_1 - C_{24} alkyl, C_1 - C_{24} alkoxy, and substituted C_1 - C_{24} alkoxy;

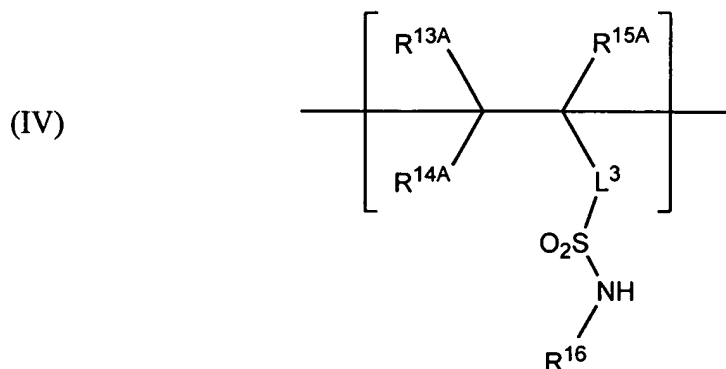
R^{14} and R^{14A} are independently selected from hydrogen, fluorine, C_1 - C_{24} alkyl and substituted C_1 - C_{24} alkyl; and

R^{15} and R^{15A} are independently selected from hydrogen, fluorine, C_1 - C_{24} alkyl, and substituted C_1 - C_{24} alkyl, and further wherein any two of R^{13} , R^{14} , and R^{15} may be taken together to form a ring and any two of R^{13A} , R^{14A} , and R^{15A} may be taken together to form a ring.

25. The process of claim 20, wherein the polymer comprises a first olefinic monomer unit having the structure of formula (II)



and a second olefinic monomer unit having the structure of formula (IV)



wherein:

m , n , and q are independently zero or 1;

L^1 is selected from C_1 - C_{12} alkylene, substituted C_1 - C_{12} alkylene, C_1 - C_{12} heteroalkylene, substituted C_1 - C_{12} heteroalkylene, and further wherein when L^1 is optionally substituted and/or heteroatom-containing C_1 - C_{12} alkylene, L^1 may be linear, branched, or cyclic;

X is selected from C_3 - C_{30} alicyclic and substituted C_3 - C_{30} alicyclic;

L^2 is selected from C_1 - C_{12} alkylene, substituted C_1 - C_{12} alkylene, C_1 - C_{12} heteroalkylene, substituted C_1 - C_{12} heteroalkylene, and further wherein when L^2 is optionally substituted and/or heteroatom-containing C_3 - C_{12} alkylene, L^2 may be linear, branched, or cyclic; and

R^1 is selected from acetal-containing and ketal-containing substituents;

L^3 is selected from C_1 - C_{12} alkylene, substituted C_1 - C_{12} alkylene, C_1 - C_{12} heteroalkylene, substituted C_1 - C_{12} heteroalkylene, C_3 - C_{15} alicyclic, C_3 - C_{15} fluoroalicyclic, C_5 - C_{14} arylene, substituted C_5 - C_{14} , C_5 - C_{14} heteroarylene, substituted C_5 - C_{14} heteroarylene, and combinations thereof;

R^{13} and R^{13A} are independently selected from hydrogen, fluorine, C_1 - C_{24} alkyl, substituted C_1 - C_{24} alkyl, C_1 - C_{24} alkoxy, and substituted C_1 - C_{24} alkoxy;

R^{14} and R^{14A} are independently selected from hydrogen, fluorine, C_1 - C_{24} alkyl and substituted C_1 - C_{24} alkyl;

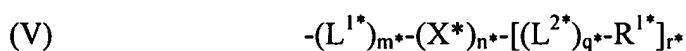
R^{15} and R^{15A} are independently selected from hydrogen, fluorine, C_1 - C_{24} alkyl, and substituted C_1 - C_{24} alkyl, and further wherein any two of R^{13} , R^{14} , and R^{15} may be independently taken together to form a ring and any two of R^{13A} , R^{14A} , and R^{15A} may be taken together to form a ring; and

R^{16} is selected from C_1 - C_{24} alkyl and substituted C_1 - C_{24} alkyl, C_1 - C_{24} fluoroalkyl and substituted C_1 - C_{24} fluoroalkyl.

26. The process of claim 20, wherein the monomer mixture further comprises at least one additional olefinic monomer.

27. The process of claim 26, wherein the at least one additional olefinic monomer is selected from (i) a monomer containing an acid-cleavable substituent R^{CL*} ; (ii) a monomer containing an acid-inert, polar substituent, R^P ; (iii) a monomer containing an acid-inert, nonpolar substituent, R^{NP} ; and (iv) combinations thereof.

28. The process of claim 27, wherein R^{CL*} has the structure



in which:

m^* , n^* , and q^* are independently zero or 1;

r^* is an integer of at least 1;

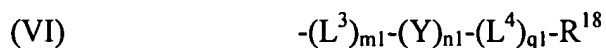
L^{1*} is selected from C_1 - C_{12} alkylene, substituted C_1 - C_{12} alkylene, C_1 - C_{12} heteroalkylene, substituted C_1 - C_{12} heteroalkylene, and further wherein when L^{1*} is optionally substituted and/or heteroatom-containing C_1 - C_{12} alkylene, L^{1*} may be linear, branched, or cyclic;

X^* is selected from C_3 - C_{30} alicyclic and substituted C_3 - C_{30} alicyclic;

L^{2*} is selected from C_1 - C_{12} alkylene, substituted C_1 - C_{12} alkylene, C_1 - C_{12} heteroalkylene, substituted C_1 - C_{12} heteroalkylene, and further wherein when L^{2*} is optionally substituted and/or heteroatom-containing C_3 - C_{12} alkylene, L^{2*} may be linear, branched, or cyclic; and

R^{1*} is selected from acid-cleavable ester, oligomeric ester, ether, carbonate, and orthoester substituents.

29. The process of claim 27, wherein R^P has the structure



in which:

m1, n1, and q1 are independently zero or 1;

L³ is selected from C₁-C₁₂ alkylene, substituted C₁-C₁₂ alkylene, C₁-C₁₂ heteroalkylene, substituted C₁-C₁₂ heteroalkylene, and further wherein when L³ is optionally substituted and/or heteroatom-containing C₁-C₁₂ alkylene, L¹ may be linear, branched, or cyclic;

Y is selected from C₃-C₃₀ alicyclic and substituted C₃-C₃₀ alicyclic;

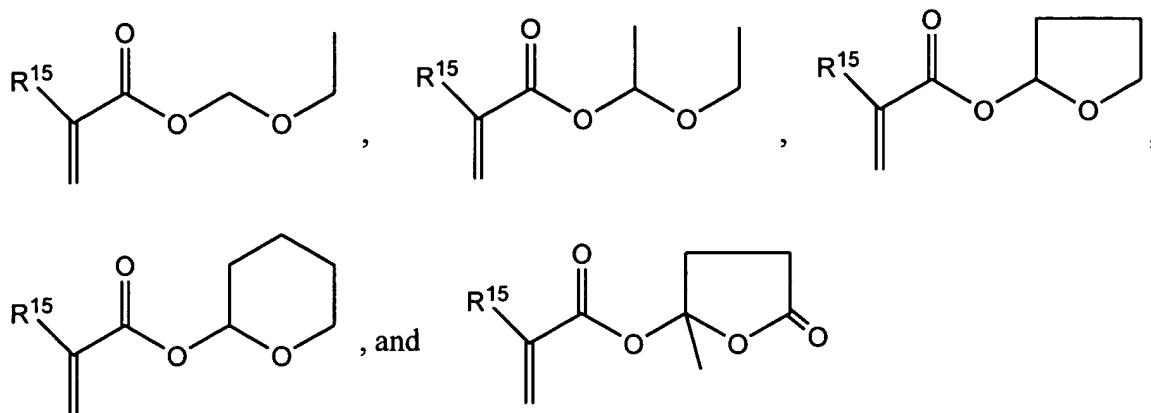
L⁴ is selected from C₁-C₁₂ alkylene, substituted C₁-C₁₂ alkylene, C₁-C₁₂ heteroalkylene, substituted C₁-C₁₂ heteroalkylene, and further wherein when L⁴ is optionally substituted and/or heteroatom-containing C₃-C₁₂ alkylene, L⁴ may be linear, branched, or cyclic; and

R¹⁸ is an acid-inert polar organic group containing a heteroatom with a Pauling electronegativity greater than about 3.00.

30. The process of claim 27, wherein R^P is selected from lactone, anhydride, sulfonamide, fluoroalkanol, alkanol, alicyclic alkanol, esters, ethers, and a combination thereof.

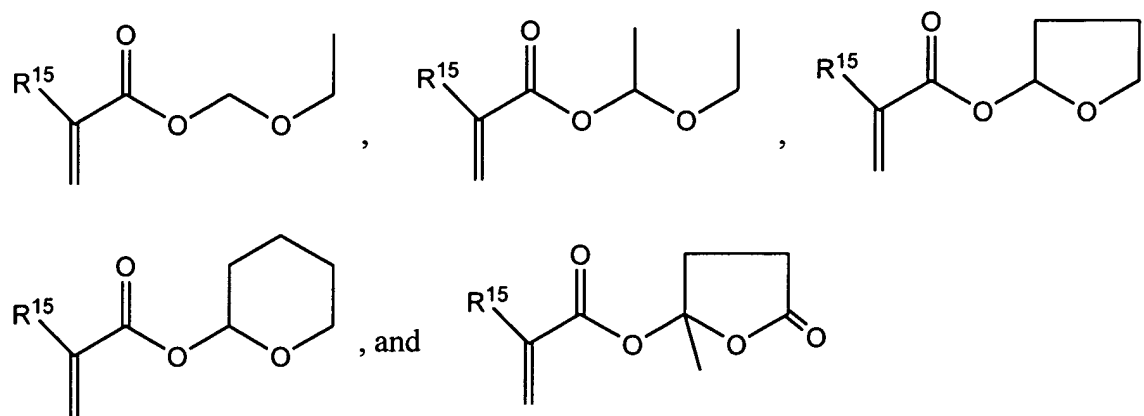
31. The process of claim 27, wherein R^{NP} is C₁-C₁₈ hydrocarbyl or fluorinated C₁-C₁₈ hydrocarbyl.

32. The process of claim 24, wherein the first olefinic monomer unit is derived from a monomer having a structure selected from the formulae



33. The process of claim 32, wherein R^{15} is selected from hydrogen, fluorine, $\text{C}_1\text{-C}_{24}$ alkyl, and fluorinated $\text{C}_1\text{-C}_{24}$ alkyl.

34. The process of claim 25, wherein the first olefinic monomer unit is derived from a monomer having a structure selected from the formulae



35. The process of claim 34, wherein R^{15} is selected from hydrogen, fluorine, $\text{C}_1\text{-C}_{24}$ alkyl, and fluorinated $\text{C}_1\text{-C}_{24}$ alkyl.